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SHOCK-WAVE SYNTHESIS OF NONSTOICHIOMETRIC ALUMINIZING SPINEL AND GAHNITE

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As the result of shock-wave impact on amorphous aluminum hydroxide placed in a brass cylinder of the preservation ampoule, it was possible to synthesize two phases with the spinel structure: $ZnAl_2O_4$ and $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$. The x-ray patterns and the lattice parameters of the obtained phases are presented.

We have earlier [1] synthesized hercynite $FeAl_2O_4$ by a shock-wave impact on aluminum hydroxide (gibbsite).

The spinel $FeAl_2O_4$ could be formed only as the consequence of the reaction between the product of aluminum hydroxide disintegration and the steel wall of the ampoule. At present we have data indicating that $FeAl_2O_4$ is the product of the reaction of aluminum oxide with wustite Fe_xO and iron:

$$Fe_xO + (1 - x)Fe + Al_2O_3 = FeAl_2O_4.$$

This process is accompanied by a decrease in the Gibbs energy ΔG [2, 3]. The following equation of the temperature dependence of Gibbs energy for the specified reaction was given in [3]:

$$\Delta G^0 = -7918 + 1.46T \ (\pm 1200 \text{ cal}). \qquad (1)$$

Oxide Fe_x is thermodynamically stable only at a temperature over 843 K. At this temperature, this oxide is formed according to a eutectoid reaction:

$$Fe + Fe_3O_4 = 4FeO.$$

The composition of wustite arising in these conditions correlates with the formula $Fe_{0.938}O$. The stoichiometric composition of FeO at any temperature is a mixture of wustite with excessive oxygen and iron.

Under high pressures, the vacancy concentration decreases. At the pressure 3.6 – 5.3 GPa and the temperature 1043 K, it was possible to synthesize wustite of a strictly stoichiometric composition with the lattice parameter (a = 4.323 Å), which is slightly larger than that of the nonstoichiometric phase [4]. Magnetite Fe_3O_4 could be formed as the consequence of the reaction of water vapor with the destroyed wall material of the preservation ampoule.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2; \ \Delta G^0_{298} = -99.7 \text{ kJ/mole}.$$

Thus, the formation of magnetite, wustite, and hercynite in a steel preservation ampoule under the shock-wave effect on gibbsite can be described by the following reaction:

$$Fe + H_2O_{(gas)} + Al_2O_3 = FeAl_2O_4 + H_{2(gas)}.$$

The variation in the Gibbs energy with increasing temperature in this case is described by the equation [3]:

$$\Delta G^0 = -5850 + 0.37T. \qquad (2)$$

The Gibbs energy at temperature 1873 K calculated from expressions (1) and (2) is equal to – 5.2 kcal/mole (– 21.77 kJ/mole). The specifics of $FeAl_2O_4$ synthesis consisted in the fact that the reactants, namely $Al(OH)_3$ and Fe from the ampoule walls before the start of the experiment, were separated. The reaction became possible only as a consequence of intense hydrodynamic mixing of the reactants in the reaction zone under the effect of a strong shock wave.

In the preset study, an attempt was made to synthesize gahnite $ZnAl_2O_4$ by the shock-wave method from amorphous aluminum hydroxide and zinc contained in the brass wall of the preservation ampoule (Fig. 1).

A sample of amorphous aluminum hydroxide weighing 0.15 g and of density 1.2 g/cm^3 was placed in a narrow (4 mm in diameter) channel *1* of a brass cylinder *2* (diameter 8 mm), which, in turn, was placed along the axis of a steel cylindrical preservation ampoule *3* (the outer diameter 13 mm). To avoid depressurization of the reaction volume, the lid *4* was screwed into the inner channel of the ampoule. A shock-wave impact was implemented via a gliding detona-

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TABLE 1

Intensity	Interplanar distance D_c, Å		
	α-Al_2O_3	$ZnAl_2O_4$	$(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$
55	3.4806	–	–
48	–	2.8612	–
48	–	–	2.8311
70	2.5503	–	–
48	–	2.4405	–
52	–	–	2.4127
40	2.3785	–	–
100	2.0854	–	–
13sh	–	1.8448	1.8448
40	1.7392	–	–
11	–	1.6509	–
13	–	–	1.6341
84	1.6015	–	–
13	–	1.5589	–
16	–	–	1.5410
10	1.5134	–	–
16	–	1.4305	–
28	1.4049	–	–
48	1.3739	–	–
11	–	1.2796	–
16	1.2398	–	–
13	–	1.2349	–

tion wave generated by the explosion of a cast charge consisting of trotyl-hexogen 40/60 alloy (density 1.7 g/cm^3, detonation speed 8.1 km/sec, detonation pressure 26 GPa). The charge weighing 97 g and 35 mm in diameter was inserted in a steel shell with wall thickness 2.5 mm.

It could be expected that as a consequence of the converging conical shock wave arising along the ampoule axis and the Mach disc formation, the pressure in the reaction zone would be 2 – 3 times higher than the detonation pressure [5].

The detonation was initiated by the explosion of an azide drop via an intermediary firing pin. To avoid the break-off effect, the lower end of the ampoule was standing on a steel disk 10 mm thick, and the whole assembly was vertically placed on a thick steel slab.

Amorphous aluminum hydroxide was obtained from aluminum chloride and ammonium solutions.

The thermogravimetric analysis of amorphous aluminum hydroxide (a derivatograph of the Paulik – Paulik – Erdey system made by the MOM company) indicated that it contained a substantial amount of water (45.9 wt.%). The non-fixed water constituted 11.3%.

The x-ray phase analysis was carried out under monochromatic radiation in a FR-552 monochromator chamber ($CuK_{\alpha 1}$ radiation). Germanium was used as the reference standard.

The x-ray patterns obtained by the photo method were measured on a IZA-2 comparator. The line intensities were evaluated by the blackening marks and converted to the 100-grade scale.

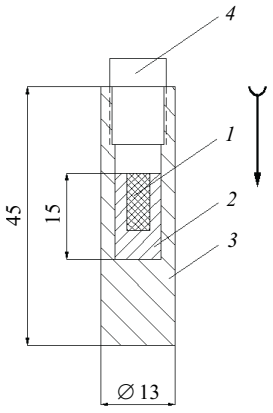

Fig. 1. Design of preservation ampoule with a brass insert.

The x-ray pattern of the products formed as the result of the shock-wave impact on amorphous aluminum hydroxide during $(2 – 3) \times 10^{-6}$ sec is shown in Table 1. The analysis of the x-ray pattern indicates that the main product of aluminum hydroxide transformation is corundum α-Al_2O_3 with unit cell parameters $a = 4.758(2)$ Å, $c = 12.999(6)$ Å. Two more phases of the spinel structure with the parameters $a = 8.094(3)$ and 8.006(2) Å are present in smaller but equal quantities.

The x-ray data of the phase with the larger lattice parameter correspond to gahnite $ZnAl_2O_4$. The interplanar distances of the second phase coincide with the distances calculated in [6] for nonstoichiometric aluminozinc spinel $Zn_{0.33}Al_{2.45}O_4$ with the parameter $a = 8.00(1)$ Å. The table does not contain the lines of the gahnite phase and nonstoichiometric aluminozinc spinel phase with $hkl = 004$ superimposed on the line of germanium with $hkl = 220$.

This phase in [6] was synthesized by calcination of crystalline mixtures of bayerite and zinc hydroxide ξ-$Zn(OH)_2$ taken in the ratio 7 : 3 for 6 h at temperature 1023 K.

As the result of refining of the structural parameters using the full-profile method of analysis and the chemical analysis data, it was found that the tetrahedral positions are fully occupied: 1/3 zinc atoms and 2/3 aluminum atoms.

The crystallochemical formula of nonstoichiometric aluminozinc spinel is $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$.

An assumption was made in [6] that part of the oxygen ions is replaced by hydroxyl groups OH^-.

Thus, it can be concluded that as the consequence of the shock-wave impact on amorphous aluminum hydroxide placed in a brass cylinder inside the preservation ampoule, two crystalline phases with the spinel structure were synthesized: $ZnAl_2O_4$ and $(Zn_{0.3}Al_{0.7})Al_{1.7}O_4$.

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